A STUDY OF FACTORS AFFECTING OPERATION OF A RADIATION CALORIMETER

By

WYNN B. FIFE

Bachelor of Science
Utah State Agricultural College
Logan, Utah
1948

Master of Science
Utah State Agricultural College
Logan, Utah
1951

Submitted to the faculty of the Graduate School of
the Oklahoma Agricultural and Mechanical College
in Partial Fulfillment of the Requirements
for the degree of
DOCTOR OF PHILOSOPHY
August, 1953

OKLAHOMA
AGRICULTURAL & MECHANICAL COLLEGE
LIBRARY
JUN 18 1954

A STUDY OF FACTORS AFFECTING OPERATION OF A

RADIATION CALORIMETER

Thesis Approved:

Thesis Adviser

Dean of the Graduate School

321667

Acknowledgement

The author wishes to express his appreciation to Dr. Irving Johnson for his advice and suggestions during the experimental investigation of the factors involved in the operation of a high-temperature calorimeter. Further the author is indebted to Dr. Johnson and other members of the faculty of the Department of Chemistry of the Oklahoma A. and M. College for their helpful criticism of this dissertation.

Mr. Gail I. Rutter, Robert T. Andersen and Charles Cole have given very valuable technical assistance in construction of various parts of the apparatus used in the study of the calorimeter.

The author also wishes to thank the Research Foundation of the Oklahoma A. & M. College who supported this research by a grant from the Office of Naval Research under contract Nonr 471(00).

Finally the author is grateful for his wife's assistance in many ways during the preparation of this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

I. INTRODUCTION

The calorimeter has long been a useful tool for the chemist in the accumulation of fundamental thermodynamic data. M. Berthelot and J. Thomsen in the late 1800's used the calorimetric method to determine the heats of formation of numerous substances and thus laid the numerical foundation on which many later thermodynamic calculations were based. Since their time, a great wealth of information (e.g., heat capacity, heat of formation, heat of fusion, heat of transition and heat of solution) necessary to the advancement of science in many fields has been accumulated by the calorimetric method.

The vacuum calorimeter, developed by Nernst and his collaborators as a means of obtaining thermal properties of matter at low temperatures, has attained great precision. However, the Nernst calorimeter has been of little value above room temperatures because of the limitations imposed by organic insulating materials and the uncertainty as to the heat loss due to radiation, which increases very rapidly with increase in temperature.

The experimental methods of high-temperature calorimetry can be classified into three broad classes: (1) The method of mixtures (2) Methods depending on heating or cooling rates (3) Methods of obtaining true specific heats directly.

The method of mixtures has reached a high degree of precision and is the one widely and frequently employed. However there are two

disadvantages inherent in this method. (1) It is not always adequate for obtaining heat effects at transition points, especially if the heats of transition are small. (2) Many substances under investigation change state on heating. On rapid cooling these substances do not revert to their original state and additional measurements of some other type are necessary to fix the heat content of the high-temperature state with respect to the lower.

Methods depending upon heating and cooling rates have also been quite widely used but according to K. K. Kelly (1) they have produced few precise results.

Numerous methods of obtaining true specific heats directly have been developed and will be discussed later in the historical section. These methods involve the measurement of the heat required to raise the temperature of the substance by a few degrees. The difficulties of the method have been discussed by White (2) who concluded that "the dropping method is more promising". However, if a widely applicable and accurate method for determining true specific heats directly were developed it would have a number of advantages over that of the method of mixtures.

Direct calorimetry can, of course, reveal minor trends in the heat capacity that are not apparent from the method of mixtures. Many transitions have small heat effects or require relatively long times to be completed. By direct methods of calorimetry, it is possible to study the following heat effects: (1) Heat capacity of metastable states (2) The effect on alloys and metals when they are changed in molecular arrangement by (a) heating and annealing (b) heating and quenching (c) cold working (3) Small heats of transition that reveal changes in

molecular or atomic arrangement of solids and liquids (4) Heats of slow reactions at high temperatures, such as the amount of heat absorbed by clay bodies during firing.

Thus, this research project was initiated to develop a direct high-temperature calorimeter. The proposed design and method of operation of the calorimeter were carefully planned to avoid the major difficulties encountered by other workers in this field.

The basic design and technique of operation were originated by Dr. Irving Johnson and William R. Willis (3). However, it was felt that refinements in apparatus and procedures were necessary to fully realize the possibilities of the calorimeter in obtaining satisfactory heat capacity data. This research is a further study of the factors affecting the operation of the calorimeter and modification of the structural features in an attempt to obtain the most precise data possible.

II. A BRIEF HISTORICAL REVIEW OF DIRECT HIGH TEMPERATURE CALORIMETRY

1. Introduction

In general, calorimeters may be classified into two types: isothermal and adiabatic. In the isothermal method the surroundings of the system (usually the outer jacket of the calorimeter) are kept at constant temperature, and the temperature of the inner vessel, the calorimeter proper, is observed at frequent intervals before, during and after the experiment. In the adiabatic method the temperature of the surroundings is kept as close as possible to that of the calorimeter vessel, so that there are no significant heat losses due to radiation, convection and conduction.

The two quantities to be determined in all calorimetric experiments are the change in the temperature during the experiment and the amount of heat exchanged. In addition, it is essential to know the amount of substance being used in the experiment.

The calorimetric method is used to determine the change in the heat content (i.e., the heat evolved or absorbed during a change taking place in a system at constant pressure or volume).

This review is limited to high-temperature, direct calorimetry of both broad classifications. High-temperature, direct calorimetry is restricted to those calorimeters which can be used above room temperature and in which the heat capacity can be measured directly.

2. Isothermal Method.

All methods for the determination of true specific heats have this in common--that heat is added in the form of electrical energy. We can divide these methods into two groups according to whether the heat is developed (a) in the sample wire itself which must therefore be an electrical conductor or (b) in a special heating filament.

An early means of determining specific heat (4) was to shape the metal into a rod and keep both ends at a constant temperature. After thermal equilibrium was established, an alternating current was sent through the rod and the specific heat computed from the temperature gradient observed by means of thermocouples. Heat losses by conduction were avoided by utilizing a layer of cotton.

Lecher (5) took a metal wire of 3-4 mm. in diameter and placed it in an evacuated porcelain tube, which was inserted in a constant-temperature oven. Holes were drilled into the wire, into which small thermocouples were placed. An elevation in temperature was caused by an alternating current. The time of current passage and amperage were measured. From these data the specific heat was calculated.

Corbino (6) and Pirani (7) also utilized a method similar to Leacher's in finding specific heat data of metals.

Worthing (8) and Behrens and Drucker (9) placed the sample in the form of a filament in a constant-temperature oven. The resistance was determined; then a measured quantity of heating current was passed through the wire. The resistance (i.e., temperature) was again determined. From the change in resistance and a knowledge of the electrical energy added the specific heat was calculated.

Gaede (10) developed the first direct calorimeter utilizing an electric heater source. The sample of metal under investigation had a cylindrical shape, and a hole in the center filled with mercury. In the mercury was suspended a copper nail (stift tag) containing a copper-constantan thermocouple electrically insulated from the nail. The copper-constantan thermocouple served as a heater and a means of measuring the change in temperature. The sample was surrounded by a thermostat.

The method of measuring specific heats, developed by Nernst and Eucken, was extended by Sucksmith and Potter (11) to 410°. They used this method to determine the specific heat of nickel and Heusler alloy.

Klinkhardt (12) constructed a novel calorimeter in which he used slow cathodic rays to heat up the sample of material whose specific heat was to be determined. He was also able to measure the specific heat of non-metals (e.g., ammonium chloride) by enclosing the sample in a metallic container to which he could supply heat in the above manner. The calorimeter proper and the source of cathodic rays were enclosed in a quartz tube which could be evacuated to at least 10^{-4}mm. of mercury. This quartz tube was enclosed in a furnace. At the beginning of each experiment, the setting of the oven coil was such that the calorimeter warned up slowly. Temperature readings were taken every half minute and when the slope of the temperature rise became constant a voltage was applied for one-half to 1 minute to the cathode. Voltage and current readings were taken during this time, and one-half minute after the switches were turned off temperature readings were taken every one-half minute for 3 to 5

minutes. Klinkhardt determined specific heats from 100° to 1000° C. and felt the method was accurate to 2.5% at 950° and about 0.9% at low temperatures.

Grosse and Dinkler (13) developed and improved a metal calorimeter for the determination of the specific heat of metals, oxides and slags up to 1250°.

A lengthy discussion of vacuum high-temperature calorimetry has been written by Carpenter (14). He developed the theoretical aspects as to the proper dimensions to make the calorimeter and then states, "an upper limit to the dimensions of the calorimeter was impcsed mainly by mechanical considerations, since the present form of calorimetry necessitates the enclosure of the calorimeter and certain other apparatus in an evacuated vessel". Thus he was only able qualitatively to follow the constructional aspects required by his extensive theory.

Essentially the calorimeter proper was a hollow cylinder of mild steel, 50 mm. in diameter by 80 mm. long, turned from a solid rod to a wall thickness of 0.5 mm. It was constructed with a screw-on lid having a diameter equal to that of the cylinder. The entire steel container was nickel plated to thickness of about 0.05 mm.

A platinum heating element was wound bifilarly in a space between the nickel-plated steel calorimeter and a silver radiation shield. The shield was held in place by 16 cheese-headed steel screws silver-soldered head down to the calorimeter, the shield being held down firmly by nuts.

The outside of the calorimeter, the inside of the silver case and the platinum wire were blackened by coating with Bakelite varnish, which was carbonized by heating in a furnace to about 350° C. The blackening was to make the emissivity of the surfaces approach that of a full radiator.

Electrical contact of the platinum heater with the calorimeter was prevented by the interposition of thin sheets of mica between the platinum wire, calorimeter and shield. Another silver radiation shield surrounded the inner shield and calorimeter. It was also in good thermal contact with the calorimeter and thus all the heat from the platinum heater should have been absorbed by the calorimeter and shields.

The calorimeter was hung by 4 cm. of 26-s.w.g. platinum wire with an insulating link in the form of a glass bead to prevent heat loss by conduction. Other heat losses by convection from the calorimeter were minimized by having the calorimeter in a vessel evacuated to 10^{-3} mm. or less.

The entire assembly was contained in a furnace made of a thick-walled copper pipe on which was noninductively wound 34-s.w.g. nichrome wire. The electrical and thermal insulation consisted of asbestos paper and asbestos wool respectively.

Newton, Kaura and DeVries (15) determined the specific heat of diphenyl using an isothermal calorimeter made from a brass cylinder of 200 cc. capacity. A screw cap, carrying a thermocouple well, a stirrer and a heating coil which extended in the form of a U nearly to the bottom of the container, was fitted to the above cylinder. A

thin copper cylinder furnished with a uniformly wound heating coil was placed around the calorimeter. There was a 0.5-cm. clearance between the two. The surroundings of this apparatus were held at constant temperature by means of a vapor jacket.

The heats of fusion and transformation of metals were determined by Kubaschewski and coworkers (16). In their method they placed the metal in a suitable crucible and heated it to just below the melting point. Then by a measured input of electrical energy they caused it to melt. Corrections were made, often several times that of the heat of fusion, making the method inaccurate.

Wittig (17) used a technique similar to that of Kubaschewski but considerably refined.

A method utilizing an evaluation of the cooling curve of metals was developed by Knappworst (18). However this method appears to be somewhat limited as it entails heating the sample in an evacuated aluminum cylinder and then placing it in a rapidly stirred ice bath to obtain the cooling curve experimentally.

3. Adiabatic Method.

Williams and Daniels (19), utilizing a direct adiabatic calorimeter, measured the specific heats of organic liquids so that they could observe the small irregularities in specific heat caused by changes in molecular form. Their calorimeter was patterned after that of Richards (20). The calorimeter of Williams and Daniels is described briefly in the following paragraphs.

The liquid to be studied was contained in a cylindrical copper vessel 8 cm. high and 6 cm. in diameter, supported in an enclosing

vessel with an air gap of 7 mm. between the two. The enclosing vessel was of copper 12 cm. high and 8 cm. in diameter, fitted with a threaded cover of bronze. The cover was fitted with an upright tube for the stirrer and with conical stuffing boxes for the admission of the heater and thermocouple. The leads for the heater passed out through small copper tubing which ran through the bath for a distance of 20 cm. to prevent thermal leakage along the wires to the cold air of the room.

A multiple thermel of five copper-constantan thermocouples was enclosed in a thin glass tube, and connected to a sensitive galvanometer. One division on the scale corresponded to 0.001° C. and the temperature of the outer bath was adjusted as far as possible to keep the galvanometer on zero. The temperature of the calorimeter was measured by means of a platinum resistance thermometer to an accuracy of 0.001° C.

The tank for the outer bath was made of copper and insulated with asbestos. The bath fluid consisted of 9 liters of glycerol containing 20 g. of ferric chloride to make it a conductor. For higher temperatures molten zinc chloride was to have been used as a bath liquid. The bath was heated externally by a resistance wire wound around the tank and internally by passing an alternating current directly through the liquid bath. A rheostat in the external heating circuit and a rheostat and switch in series with the electrolytic circuit allowed efficient temperature control.

A suitable volume (160 cc.) of purified liquid was accurately weighed and added to the calorimeter. A measured amount of electrical energy was passed for a given time interval through the internal

calorimeter heater. The heating raised the liquid temperature about 5°.

The water equivalent of the calorimeter was determined and used in the calculation of the specific heat of the organic liquids.

Kangro (21) developed an adiabatic calorimeter for the measurement of specific heat of solids at high temperatures. He stated that the principle of adiabaticity demanded that the temperature alteration of the calorimeter be followed rapidly by its surroundings. Therefore, he utilized a ring oven controlled by a vacuum tube arrangement fed by two platinum resistance thermometers in the calorimeter and four in the oven.

A great deal of work on specific heat, phase transitions, and order-disorder phenomena was done by Sykes and his coworkers (22, 23, 24, 25, 26, 27). Initially he devised an apparatus in which the metallic test piece, in the form of a cylinder, and a copper piece of the same dimensions were mounted on heat-insulating supports in symmetrically situated cavities in a copper block. This block was placed in a nichrome-wound furnace. However, no way was discovered of equalizing the emissivity of the specimen and copper sample at all temperatures and this with other difficulties caused Sykes to abandon the method as a means of obtaining absolute specific heats.

In its place he developed another apparatus. The calorimeter contained the specimen in the form of a hollow cylinder, solid on one end and closed at the other by a lid. The hollow space in a cylinder contained a heater in the form of a spiral, from which the heat was transmitted entirely by radiation. This hollow cylinder was mounted inside a copper cylinder also solid at one end and closed by a lid at

the other. The calorimeter was contained in a silica tube which could be evacuated to 10^{-3} mm. or less. The entire apparatus was then placed in a tubular resistance furnace.

The method of operation was to bring the furnace and calorimeter to an equilibrium condition initially at the desired temperature. At this time the power input to the furnace was adjusted so that the copper cylinder was heated at a uniform rate according to the line C_{T_B} (Fig.1). Then by suitable manipulation of the power input to the heating coil the temperature of the specimen was made to follow the curve C_{T_S} (Fig.1).

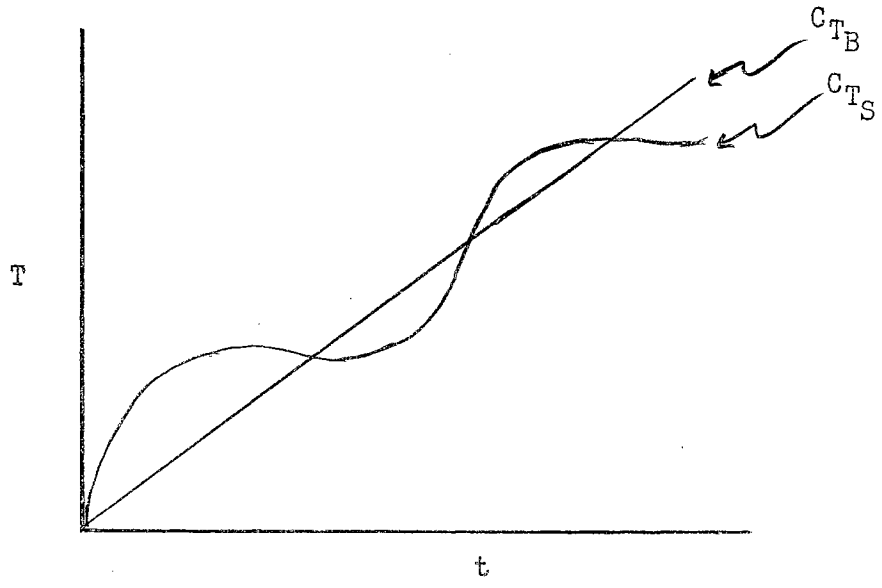


Fig. 1. Temperature vs. Time Curve (Sykes)

At the points of intersection of the two curves, where $T_S = T_B$, no external heat was received by the specimen. Thus the following equation should be valid;

$$Q = MC_p\left(\frac{dT_S}{dt}\right)_{T_S = T_B}$$

where Q is the power supplied to the coil; M is the mass of the

specimen, C_p is the instantaneous specific heat at the temperature T_S and t the time in minutes.

Moser (28) developed an abiabatic calorimeter similar to that of Sykes which had an accuracy of about 0.5% in measurements in the range of 50° to 670° C. The true specific heat C_p of a sample of mass m was calculated from the relationship.

$$C_p = \frac{1}{m}\left[\frac{0.239 \times E \times I - a}{\Delta\vartheta} - W\right]\frac{1}{1 + b}$$

where W is the water equivalent of the empty calorimeter; a and b are corrections for the loss of heat during measurements and for the difference between the increase of temperature of the calorimeter and the sample; $\Delta\vartheta$ is the temperature change of the calorimeter; E is voltage and I is the current.

A calorimeter to measure the latent energy due to cold working of metals was designed and constructed by Quinney and Taylor (29). It is very similar in principle to that of Sykes.

Theoretically a spherically shaped furnace is the most desirable because a sphere presents the least surface for heat leakage for a given volume of material and because of its symmetry. Therefore Winkler (30) designed an adiabatic calorimeter of this shape.

The platinum spheres (i.e., calorimeter and shield) were made of hemispheres with friction seals. The inner sphere is supported in the outer by a tripod of quartz tubes. The outer sphere rests on the tips of pieces of rounded quartz rod. The furnace is of Alundum cement and is heated with a uniform nichrome wire winding. The internal calorimeter platinum heater wire is contained in a hollowed-out ball of Nichrome V and cemented in place with fine Alundum.

Stow and Elliot (31) constructed a rugged calorimeter that gave an accuracy of about 0.5% up to temperatures of 300° for use in determining the specific heat of rosin and its derivatives.

Armstrong (32) constructed an adiabatic calorimeter to operate on Moser's principle. The material whose specific heat was to be measured was fitted into a copper cone (the calorimeter) in the form of a machined solid or closely packed powdered pieces. The sample and container were heated by a calorimeter heating element centrally located and running the entire length of the sample container. The calorimeter proper was completely surrounded by a radiation jacket which was kept as nearly as possible at the same temperature. The jacket was supported by a perforated steel tube and enclosed in a furnace which could be evacuated or filled with an inert gas. The calorimeter was constructed primarily to study the atomic heat of the transition metals from chromium to nickel. It was said to have an accuracy of 1% or better from 400° to 600° C.

A study of the formation of alloys was made by McKisson and Bromley (33). To do this they designed a high-temperature adiabatic calorimeter that could be used between 600° K. and 1500° K.

The specific heat of high polymers was studied by Malcolm and his coworkers (34). The calorimeter was of rectangular construction but Malcolm felt that a more symmetrical shape was desirable, and work was in process in constructing a new calorimeter having a cylindrical shape. The temperature range of the calorimeter was -20° to 300° C. with a precision of 0.5 to 0.6%, but the author felt that the absolute error was of the magnitude of 1 to 2%.

III. APPARATUS

The radiation calorimeter constructed by Dr. Irving Johnson and William R. Willis was used to study the factors affecting its operation. Essentially this radiation calorimeter consisted of four main components: (a) calorimeter proper (b) shield furnace (c) vacuum system and (d) electrical components. A detailed description of this apparatus may be found in Mr. Willis's thesis (3).

A brief description of the radiation calorimeter is contained in the following sections. The modifications and additions will be discussed in detail.

1. Calorimeter.

The calorimeter was as nearly a perfect sphere as one could turn on a metal lathe. A one-half inch-diameter hole was drilled into the sphere to such a depth that the internal heater would lie at the center of the sphere. A one-half inch hole was threaded and a threaded plug made. One end of the plug was hollowed out to accommodate the internal heater. Two holes in the plug led from the heater to the outside and accommodated one-eighth inch pipestem that insulated the heater leads from the calorimeter and the shield. The internal heater form, made of lava, was a hollow cylinder 9/16" long and 7/16" in diameter, with a wall thickness of 1/16". A double thread was cut on the exterior of the heater form and the heater wire (Nichrome B & S # 28) was wound in the grooves of the thread. From

the heater to the outside were copper wire leads (B & S # 28), which were silver-soldered to the nichrome wire winding. The inside space of the internal heater form was filled with a solid plug of the same material as the calorimeter. This plug was made so that its ends were in contact with the calorimeter.

A graphite calorimeter was made having the following physical characteristics:

Wt. of graphite sphere	112.8684 g.
Wt. of graphite heater plug	0.4430 g.
Total wt. of graphite	113.3114 g.
Wt. of lava heater form	1.5800 g.
Wt. of Nichrome heater wire	0.2484 g.
Wt. of two 1 19/32" pipestems	0.5315 g.
Wt. of two 4" pieces of # 28 Cu wire	0.1448 g.
Diameter of graphite sphere	1.960±0.0002 in.

A photograph of this calorimeter disassembled is shown in Fig. 2.

2. Shield furnace.

The hemispherical form for the shield furnace used previous to these experiments, was made of fire clay. When this form was fired it shrank and warped so that the interior of the finished furnace was no longer spherically symmetrical. In addition, it was difficult to obtain two hemispheres that would fit together smoothly at the equator.

To overcome these difficulties the outer shield furnace of the calorimeter was made in the following manner. Two hollow graphite hemispheres having an outside diameter of $4\frac{1}{4}$" were turned on a lathe. The wall thickness was $\frac{1}{4}$". The edges of the hemispheres were turned so that one had a groove, the other a lip; this arrangement made a snug fit to completely enclose the calorimeter with a concentric, spherical surface. The bottom hemisphere contained three pointed

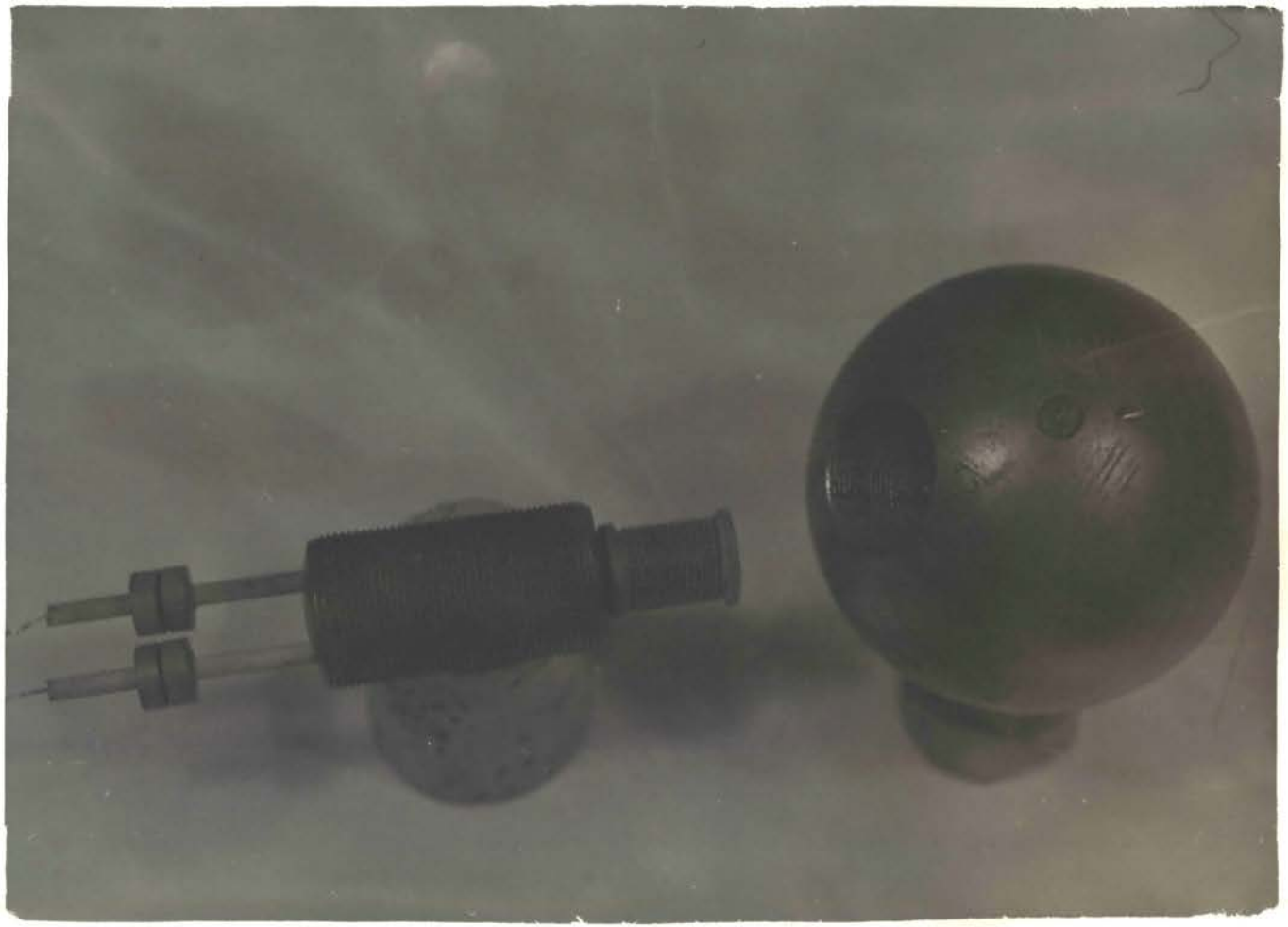


Fig. 2 Calorimeter and Internal Heater

supports of lave (Fig. 3) on which to place the calorimeter. These supports separated the calorimeter from the shield electrically and thermally. They were constructed and located in such a manner that the calorimeter was supported in the center of the hollow graphite sphere.

Alundum cement (RA 162) was mixed with water until plastic. A layer about $\frac{1}{4}$" thick was then spread uniformly over the outside of the graphite hemisphere and allowed to air dry. The hemisphere was then placed in the lathe, turned down to an even surface, and machined with a loxodrome groove. A Nichrome heater (B & S # 18), its shape preformed by annealing it in a loxodrome groove (Fig. 4), was placed over the Alundum cement and tied in position with string. Another layer of Alundum cement about $\frac{1}{2}$" thick was placed over the whole and allowed to air dry. The hemisphere was again mounted on the lathe and the Alundum coating turned to a uniform thickness. The top hemisphere then had four 1/8" holes drilled into it at such angles that the calorimeter could not "see" the outside. These holes made possible the rapid evacuation of the interior of the shield furnace. At the equator, four other holes were drilled to allow the thermocouple and heater leads to pass through the shield. The alundum was then cured by heating it in a muffle furnace to 1100° C., care being taken to exclude air to minimize oxidation of the graphite. For views of the furnace and mounted calorimeter see Fig. 5, 6.

3. Vacuum System.

The vacuum system was made of steel pipe. The main container had an outside diameter of 10 7/8" with a wall 7/8" thick and flanges welded to each end having a 5/16" by 1/32" groove cut in them. A

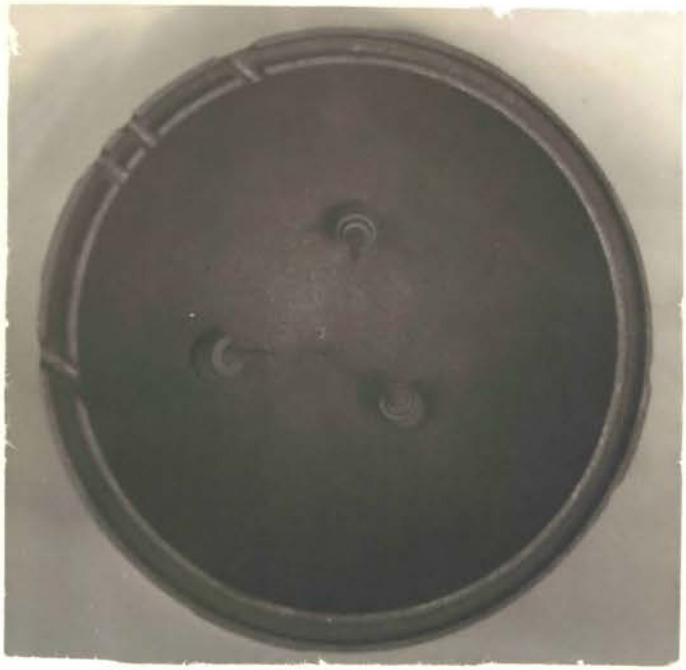


Fig. 3 Graphite Liner and Lava Supports

Fig. 4 Loxodrome Groove

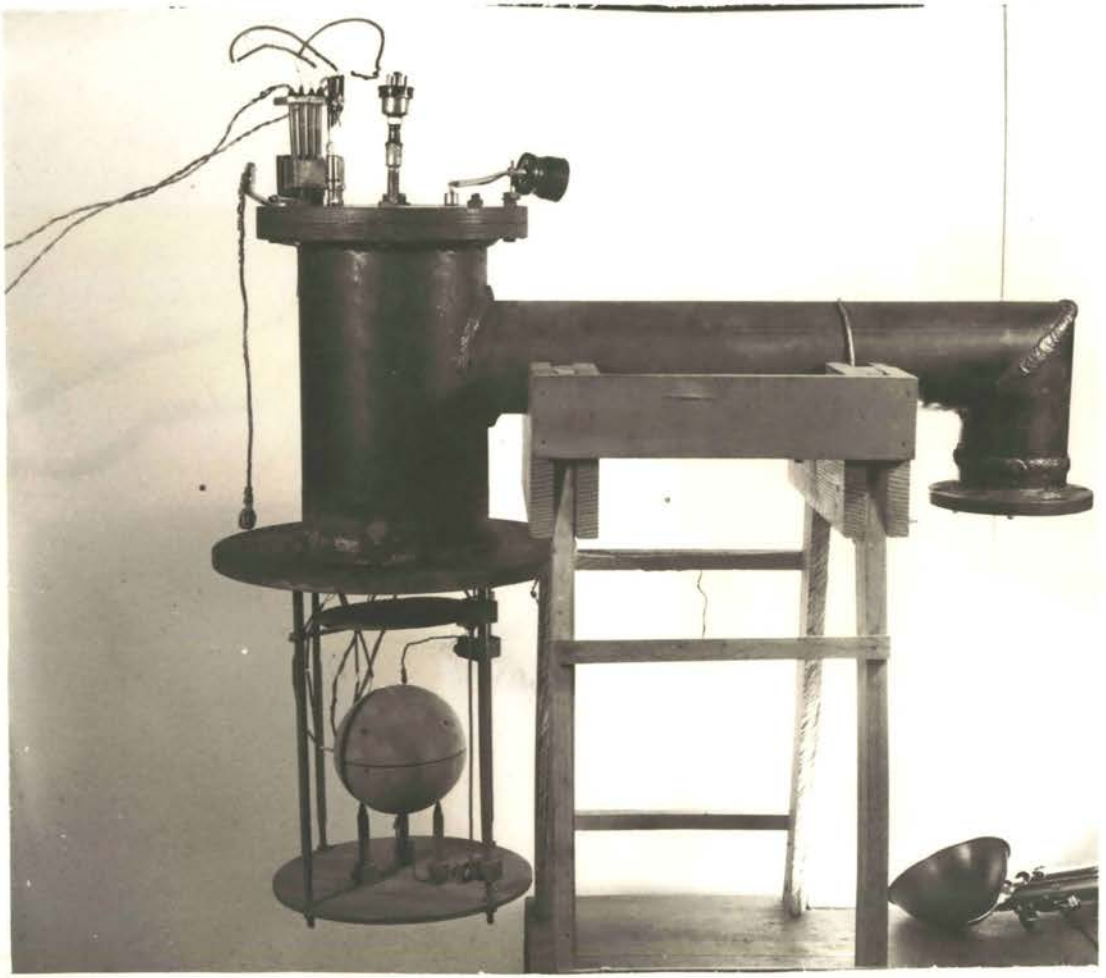


Fig. 5 Assembled Shield Furnace

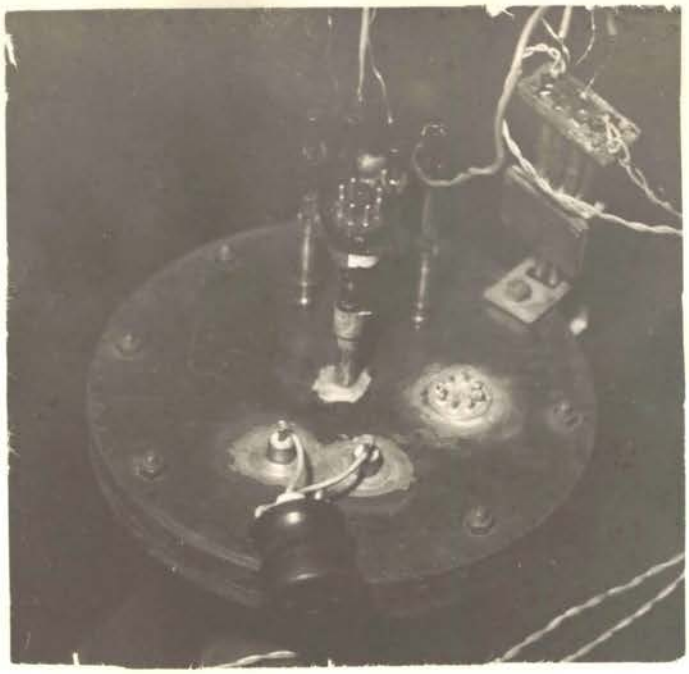


Fig. 7 Electrical Leadins to Vacuum System

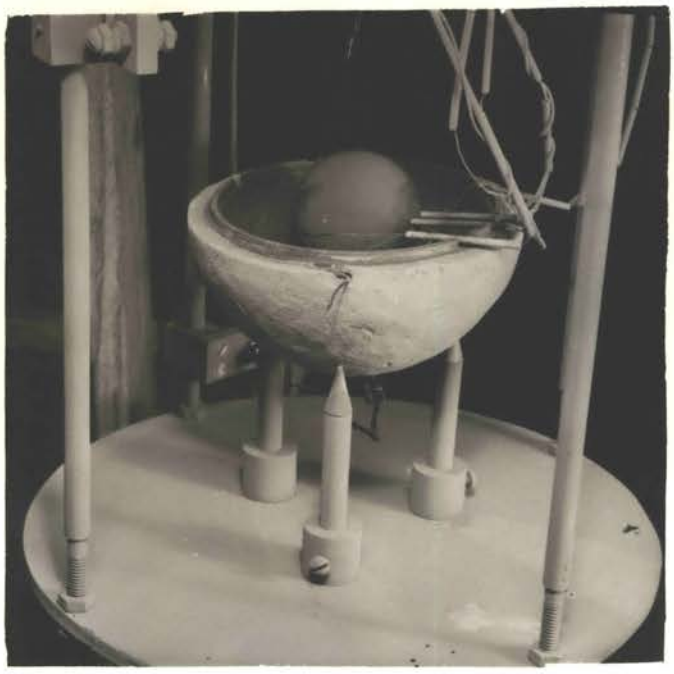


Fig. 6 Shield Furnace Showing Installed Calorimeter

butyl rubber gasket was placed in the groove and the top and bottom plates bolted into position. The upper part of the vacuum system consisted of a pipe 6 5/8" in outside diameter, 6" in inside diameter and 11" high. The bottom was welded to the top plate of the main container of the vacuum system. The top, which was bolted on, contained the electrical power, potential measuring and thermocouple leadins Fig. 7. From the center of the upper pipe a 6" steel pipe led to the diffusion pump (Distillation Products, Inc. Type MC-275). A one-inch copper pipe connected the diffusion pump to the fore pump (Cenco MegaVac Pump). The pressure at the fore pump was measured with a Hastings Vacuum Gauge. At the top of the vacuum container, the pressure was measured using a Philips Gauge (Type PHG-1). It was possible to obtain a vacuum of 0.01 micron with the shield furnace at 20° C. and 0.1 micron with the shield furnace at 600° C. In order to operate the vacuum system continuously a pressure switch (Penn type 270BP10 model 4404) was installed to control the diffusion pump heater current. If the water pressure was insufficient to insure proper cooling of the diffusion pump, the electric current to the diffusion pump heater was automatically shut off.

During operation of the calorimeter, the main container of the vacuum system was submerged in a water bath, in which water was continuously circulating, to remove the heat radiated from the shield furnace. It was necessary to maintain a constant bath temperature during a complete experiment because a change in bath temperature would cause a corresponding change in the shield furnace temperature. Initially the water was shut off at night because the regular overflow

pipe was not adequate to handle the increased water flow caused by increased night water pressure. When the water was turned on again in the morning about 4 to 6 hours were required to stabilize the bath temperature. In order to overcome this difficulty, a float-controlled on-off switch was installed. This switch in the "on" position (low water level) activated a valve in the water line allowing the water to flow into the water bath. If the water reached a mark 1 inch below the top of the bath, the float was raised and the switch changed to the "off" position causing the valve in the water line to shut the water off.

4. Electrical components.

(a) Temperature measurement.

The temperature of the calorimeter was measured with a thermocouple, a Leeds and Northrup Potentiometer No. 7552 and a L & N Galvanometer No. 2284 (sensitivity 0.045 μv/mm). This galvanometer replaced the original L & N Galvanometer (sensitivity 0.41 μv/mm) used by Mr. Willis. Use of a more sensitive galvanometer was necessary to increase the precision in determining the time necessary for the calorimeter to cool 1 micro-volt. The shield temperature was measured with the same type of thermocouple but a L & N Potentiometer No. 316493 and a L & N Galvanometer No. 2430 (sensitivity 0.41 μv/mm) were used. The hot junctions of the thermocouples were placed in a hole in the calorimeter and shield and held in place by a set screw. The cold junction and junction with the copper leads were contained in a copper junction box that was kept at a constant temperature in a Dewar flask containing crushed ice and distilled water.

(b) Calibration of the thermocouples.

The Pt to Pt 13% Rh thermocouples used in these experiments were calibrated according to the procedure outlined in the National Bureau of Standards Bulletin (35). Listed in Table 1 are the NBS metals used in the calibration also listed is the deviation from the melting points given by NBS.

Table 1 Thermocouple Calibration

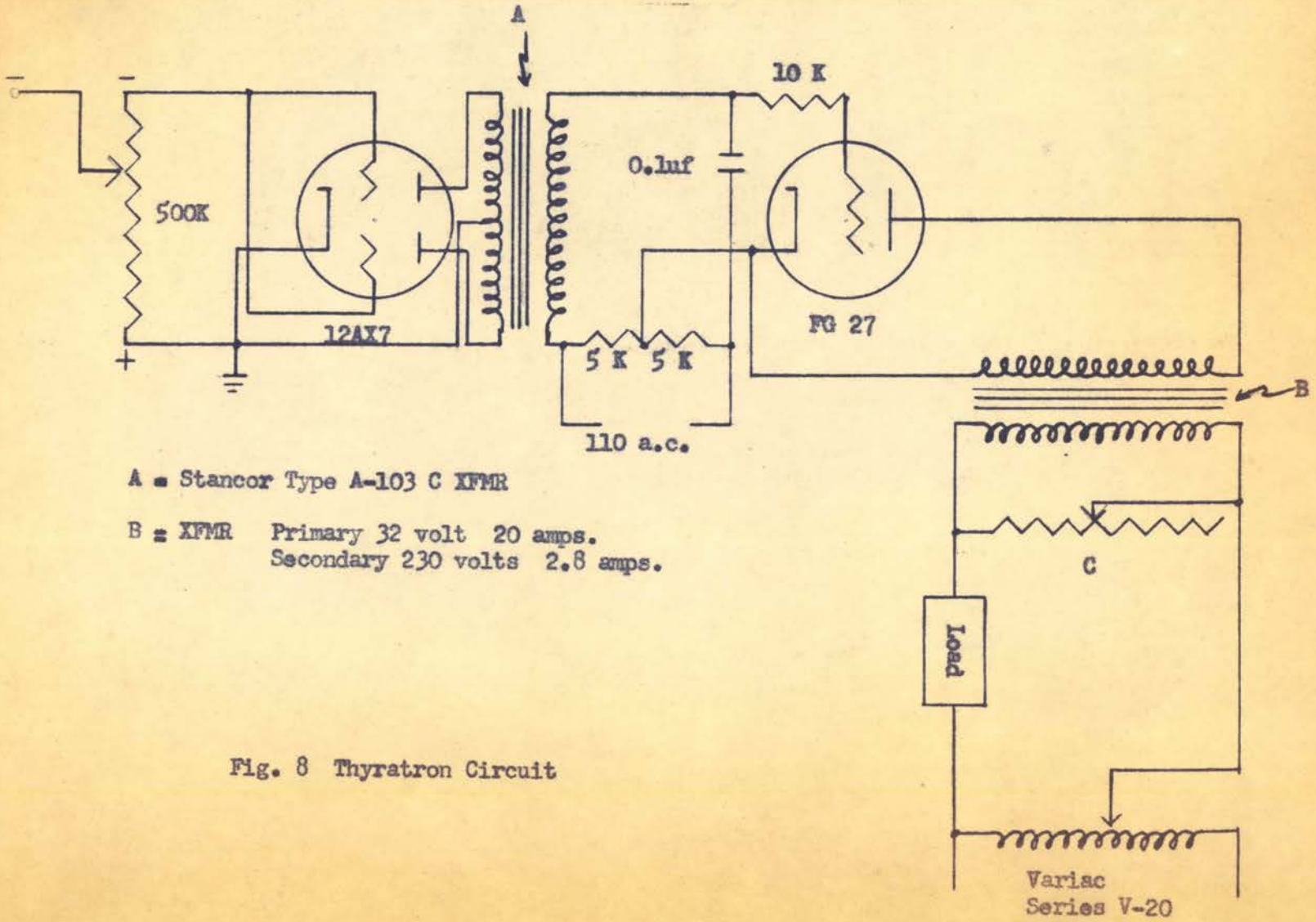
Metal	Thermocouple	M.P.° C	emf (mv) calc.	emf (mv) obs.	diff (μv)
Tin	T_c	231.9_0	1.7504	1.7490	-1.4
	T_s			1.7490	-1.4
Lead	T_c	327.3_1	2.6624	2.6607	-1.7
	T_s			2.6596	-2.8
Zinc	T_c	419.5_0	3.6000	3.5986	-1.4
	T_s			3.5987	-1.3
Aluminum	T_c	659.7_2	6.2479	6.2470	-0.9
	T_s			6.2488	+0.9

(c) Shield heater and temperature control.

The shield current was obtained from a controlled 117 volt source (Stabaline Voltage Regulator Type EM4106). An electronic regulator (Stabaline Voltage Regulator Type IE5101) was used in the last three experiments. The electronic regulator was a more nearly constant source of current than the electromagnetic type previously used. The electronic voltage regulator was used to see if a periodic drifting of the shield heater was caused by slight changes in voltage from the supposedly constant voltage source (Stabaline Type EM4106). The periodic drifting of the shield heater was eliminated by use of the electronic voltage regulator and better control of the shield temperature was made feasible.

The voltage input to the shield heater was varied by use of a General Radio Co. Variac (series V-20). To maintain the shield constant at any given temperature a thyratron control circuit (designed and constructed by Mr. Charles Cole) was utilized. The grid bias voltage on the thyratron tube was controlled manually by using a Variac (series V-10) to vary a voltage from the constant voltage transformer. The voltage from the Variac was fed to an "Electropak" which converted the alternating current to a pulsating direct current that was used to bias the thyratron tube. The thyratron tube controlled the current through transformer B Fig. 8. The bias controlled the length of time the thyratron tube fired (i.e., current flowed from cathode to plate) and therefore the current that flowed in transformer B. When current flowed in transformer B it effectively shorted out the resistance C allowing more current to go through the load (i.e., shield heater).

Attempts were made to keep the shield temperature constant automatically. Initially the e.m.f. from the shield thermocouple was amplified and used to provide the signal bias to the thyratron tube. However the sensitivity of this method was insufficient to permit control of the shield within the desired temperature tolerance (±0.01 degree). To increase the sensitivity the e.m.f. from the shield thermocouple was balanced against a potentiometer circuit. A galvanometer L & N No. 2430 was used as the null-indication instrument. Two photo tubes were placed in front of the galvanometer in such positions that at the null point equal amounts of light fell on each photo tube, which in turn kept a constant bias on the thyratron tube. If the temperature of the shield changed, the galvanometer would drift from the null point and one photo tube would receive



A = Stancor Type A-103 C XFMR

B = XFMR Primary 32 volt 20 amps.
Secondary 230 volts 2.8 amps.

Fig. 8 Thyratron Circuit

more light causing an unbalance and changing the bias on the thyratron in such a manner as to cause the temperature of the shield to return to normal and bring the galvanometer back to the zero point. This method also failed because of the inertia of the shield to change. The shield therefore oscillated about the correct temperature but the oscillations were large in magnitude (0.1°) and thus the control was useless for our purposes.

(d) Internal heater.

The internal heater obtained its current from three 6-volt automobile batteries connected in parallel in place of the single battery initially used. This voltage source (3 batteries in parallel) gave a more nearly constant current to the calorimeter heater.

The heater circuit was simplified to eliminate as many connections as possible. The new circuit is diagramed in Fig. 9 below.

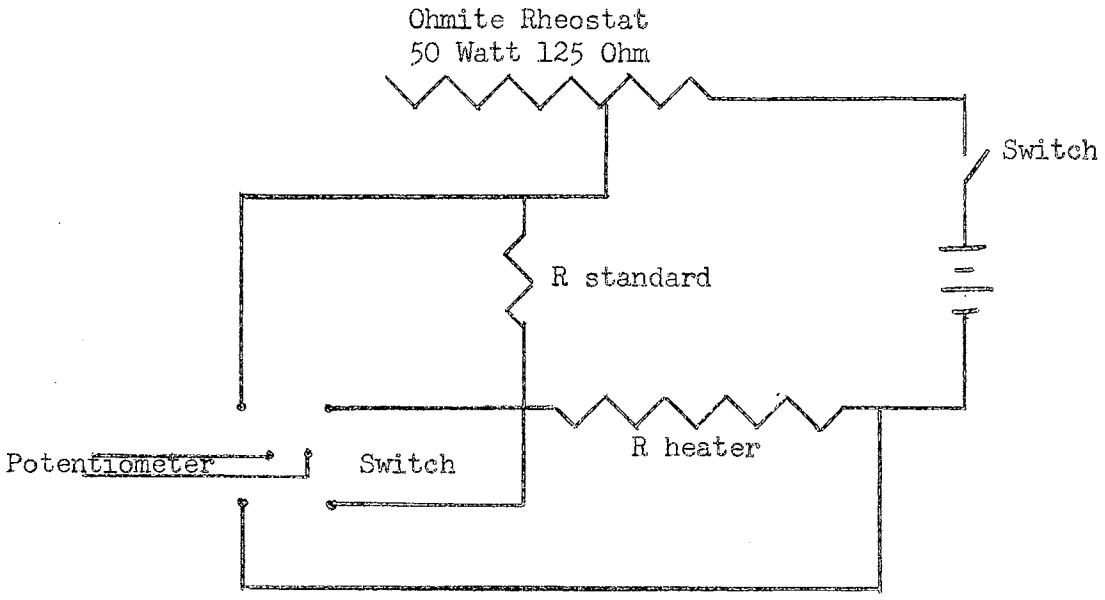


Fig. 9 Internal Heater Circuit

The voltage input was varied by use of an Ohmite Rheostat potentiometer (50-watt Model J series A). The current was determined by measuring the voltage drop across a standard resistance (4.9711 ohms) wired in series with the internal heater. The L & N potentiometer and L & N galvanometer utilized in measuring the e.m.f. from the calorimeter thermocouple were used in this measurement by use of knife switches to change from one circuit to the other.

IV. THEORY OF CALORIMETER

1. Fundamental equation of calorimeter.

The basic equation which describes the operation of the calorimeter may be written:

$$q_{ic} - C_p' \frac{dT_c}{dt} = q_{cs} \qquad (1)$$

where q_{ic} is the rate at which heat is being supplied from the internal heater, $C_p' \frac{dT_c}{dt}$ the rate at which heat is being stored by the calorimeter, and q_{cs} the rate at which heat is being lost by the calorimeter to the shield. C_p' is the total heat capacity of the calorimeter, T_c is the temperature of the calorimeter in degrees kelvin, and t is the time in seconds.

2. Heat transfer equation.

A spherical calorimeter will transfer heat to an enclosing spherical shield according to the equation:

$$q_{cs} = \sigma A g(T_c^4 - T_s^4) + K_N(T_c - T_s) \qquad (2)$$

q_{cs} = heat transferred from calorimeter to shield.

σ = 1.36×10^{-9} cal/sec. deg.^{4} cm.^{2} (Stefan-Boltzmann const.)

A = surface area of the inner sphere.

$$g\,(36) = \frac{e_c \times e_s}{e_s - e_c\,(1-e_s)(R_c^2/R_s^2)}$$

where e = emissivities of the surfaces involved.

R = radii as shown in Fig. 10.

T_c = temperature of the surface of calorimeter.

T_s = temperature of the inner surface of the shield.

K_N = the thermal conductivity of the calorimeter supports, thermocouple wire, heater wire and pipestem.

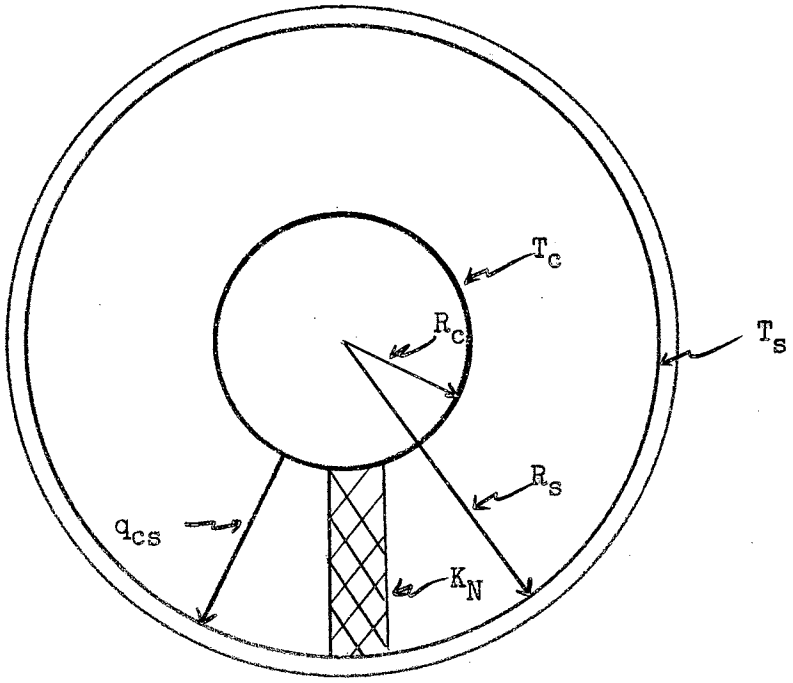


Fig. 10. Schematic of Heat Transfer

The term $\sigma A g(T_c^4-T_s^4)$ (37) represents the heat transfer due to radiation and $K_N(T_c-T_s)$ (37) that due to Newtonian conductance.

The following identity can be proven:

$$(T_c^4-T_s^4) \equiv 4T_a^3 (T_c-T_s) + T_a (T_c-T_s)^3 \qquad (3)$$

where T_a is equal to $\frac{T_c+T_s}{2}$. Since $T_a(T_c-T_s)^3$ is very small compared with $4T_a^3(T_c-T_s)$, one may write for equation (2):

$$q_{cs} = (4\sigma A g T_a^3 + K_N)(T_c-T_s) \qquad (4)$$

This equation will be valid for the heat transfer, if the heat is conducted away from the surface of the sphere only by radiation and conduction (i.e., if the pressure is low enough inside the shield furnace that heat transfer by convection is negligible).

Thus for a small range of temperature (so that T_a does not vary greatly) the rate of heat transfer is directly proportional to the difference in temperature of calorimeter and shield.

3. Operational Procedure.

(a) Calibration.

After the calorimeter had been assembled and the system evacuated the shield heater was set at a specific voltage (i.e., temperature) and the system allowed to reach steady state conditions. The temperature of the shield furnace and calorimeter proper were then recorded. A constant, measured amount of current was then passed through the internal heater circuit causing the temperature of the calorimeter to increase. The shield furnace temperature was maintained at a constant value by adjusting the bias on the thyratron

tube which controlled the current input to the shield furnace. When the temperature of the calorimeter had become constant, the heat being supplied to the calorimeter was equal to the heat being lost by the calorimeter to the shield. Thus from equation (4) one can write:

$$q_{ic} = q_{cs} = (4\sigma A_g T_a^3 + K_N)(T_c - T_s) \qquad (5)$$

where q_{ic} is the heat transferred by the internal heater to the calorimeter. The temperature of the shield and calorimeter were recorded at this steady state. Then the current to the internal heater was increased and a new steady state reached. This procedure was repeated several times, each time the temperature of shield and calorimeter and the values of the voltage drop across the internal heater and standard resistance were measured and recorded.

When q_{ic} is equal to zero and a steady state exists, $T_c = T_s$, and if we keep the shield constant at this temperature we may write

$$(T_c - T_s) \equiv (T_c - T_c^{\circ}) = \Delta T_c \qquad (6)$$

and equation (5) becomes

$$q_{ic} = (4\sigma A_g T_a^3 + K_N)\,\Delta T_c \qquad (7)$$

Therefore, for a narrow range of T_a, one would expect q_{ic} to be a linear function of ΔT_c. Since the maximum value of ΔT_c obtained during a calibration is about 5° C, the maximum variation of T_a^3 would be 1.5% at 500° K and less at higher temperatures.

Utilizing the typical calibration data in Table 2 one can calculate values for q_{ic} and show that a q_{ic} vs ΔT_c plot is a straight line.

Table 2. Calibration data. Graphite calorimeter. Temperature 743.2° K.

T_c(mv)	T_s(mv)	E_H(volts)	E_{std} (volts)	q_{ic}cal/sec	$T_c - T_c^o$	corrected* ΔT_c
4.1331	4.15	0.0	0.00	0.0	0.0	0.0
4.1485	-0.2μv!	2.2555	1.9225	0.20851	15.4	15.2
1.1628	-0.5μv!	3.0654	2.6115	0.38495	29.7	30.1

*Corrected for drift of shield temperature from the initial value.

!Shield correction.

Fig. 11 on the following page shows the plot of the above values of q_{ic} vs ΔT_c. The calibration data was fitted to a straight line $q = q_o + k_{cs}\Delta T$ by the least square method. The equations used to calculate the values of q_o and k_{cs} were:

$$q_o = \frac{[q\Delta T][\Delta T] - [q][\Delta T^2]}{[\Delta T]^2 - n[\Delta T^2]} \tag{8}$$

$$k_{cs} = \frac{[\Delta T][q] - 4[q\Delta T]}{[\Delta T]^2 - n[\Delta T^2]} \tag{9}$$

where n = number of observations

$$k_{cs} = 4\sigma A g T_a^3 + K_N$$

(b) Cooling curve.

After the last calibration data had been recorded, a cooling curve was obtained in the following manner. At the simultaneous activation of an electric timer and the switching off of the current to the internal heater, the potentiometer reading was recorded as the zero point on the cooling curve. By decreasing the potentiometer

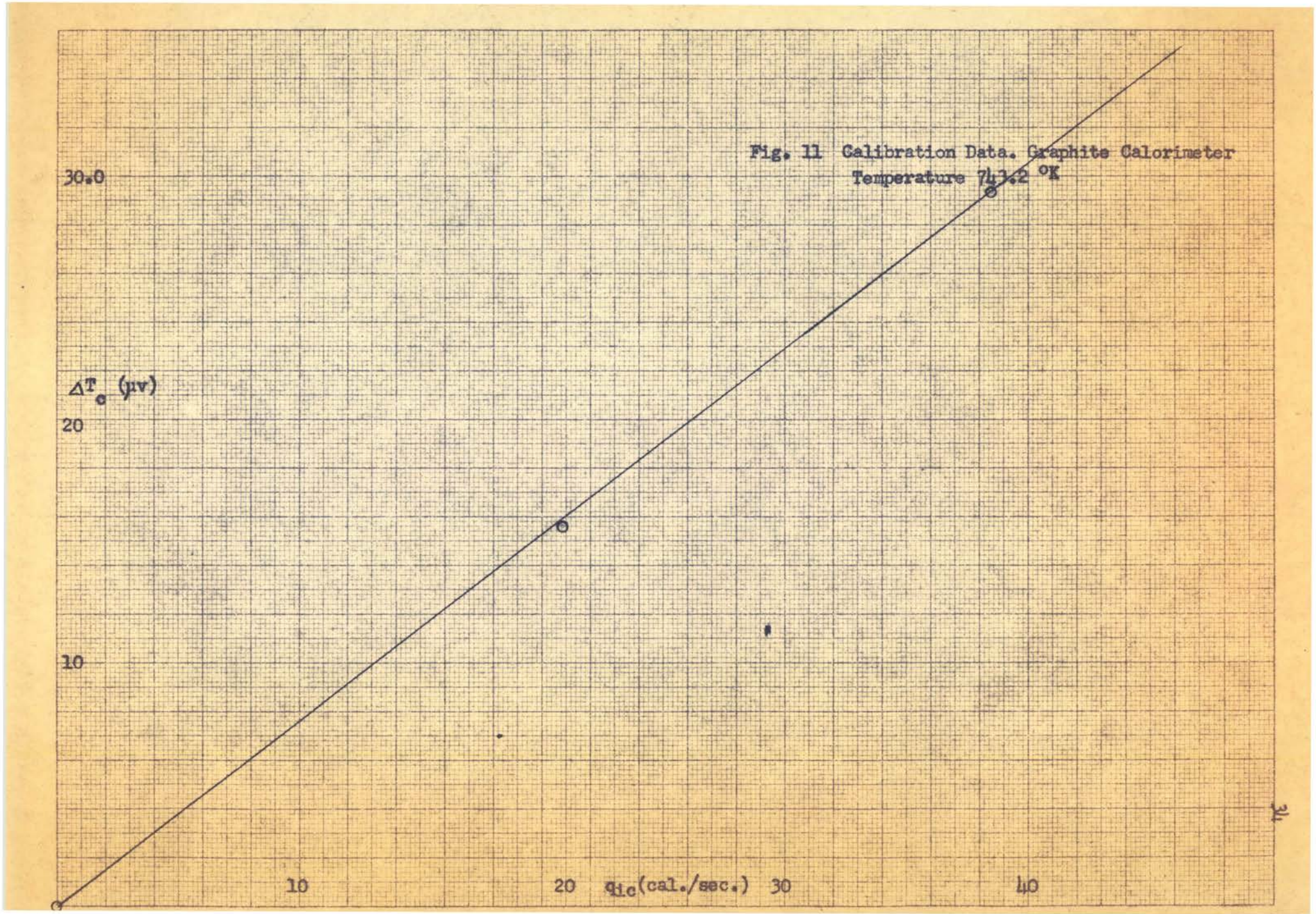


Fig. 11 Calibration Data. Graphite Calorimeter
Temperature 743.2 °K

setting 1 microvolt the galvanometer swung to the right of the zero point. As the temperature of the calorimeter decreased the galvanometer returned towards zero. At the null point the time and potentiometer readings were recorded. This process was repeated to obtain a series of time and potentiometer readings.

At the same time that one operator was obtaining the cooling curve data, another operator was adjustment the current input to the shield furnace in order to keep the shield temperature constant.

From equation (1) we note that when the internal heater current is turned off $q_{ic} = 0$ and the basic equation for the cooling of the calorimeter becomes:

$$- C_p' \frac{dT_c}{dt} = q_{cs} \tag{10}$$

This equation is valid if (a) there is no heat barrier between the internal heater and the calorimeter (i.e., they will both be at the same temperature) and (b) no temperature gradients exist in the calorimeter (e.e., all components are perfect conductors).

Thus for the cooling of a perfectly conducting sphere we may write from equations (7) and (8):

$$- C_p' \frac{dT_c}{dt} = q_{cs} = (46AgT_a^3 + K_N)\Delta T_c$$

and

$$- C_p' \frac{dT_c}{dt} = (46AgT_a^3 + K_N)\Delta T_c \tag{11}$$

Let $k_{cs} = 46AgT_a^3 + K_N$, which has been shown to be approximately constant over small temperature ranges. Thus

$$- C_p' \frac{dT_c}{dt} = k_{cs}\Delta T_c = k_{cs}(T_c - T_c^{\circ}) \tag{12}$$

T_c° is constant and thus we can integrate equation (12) to obtain:

$$\ln(T_c-T_c^{\circ})_{t=t} = \ln(T_c-T_c^{\circ})_{t=0} - \frac{k_{cs}}{C_p'} t \qquad (13)$$

or

$$(T_c-T_c^{\circ})_{t=t} = (T_c-T_c^{\circ})_{t=0} e^{-\frac{k_{cs}}{C_p'} t}$$

A plot of $\ln(T_c-T_c^{\circ})$ vs t will give a straight line whose slope is given by k_{cs}/C_p', or if $T_c-T_c^{\circ}$ is plotted vs t an exponential curve will be obtained.

Figures 12 and 13 are plots of the experimental data contained in Table 3.

Table 3. Cooling data. Graphite calorimeter. Temperature 743.2°K. T_c° 4.1331.

t (sec)	T_c(mv)	t(sec)	T_c(mv)
0	4.1628	264	4.1590
26	4.1625	286	80
42	20	308	70
62	10	332	60
77	4.1600	358	50
93	90	386	40
109	80	416	30
123	70	451	20
140	60	491	10
155	50	531	4.1400
172	40	583	90
187	30	637	80
207	20	706	70
225	10	785	60
224	4.1500	894	50

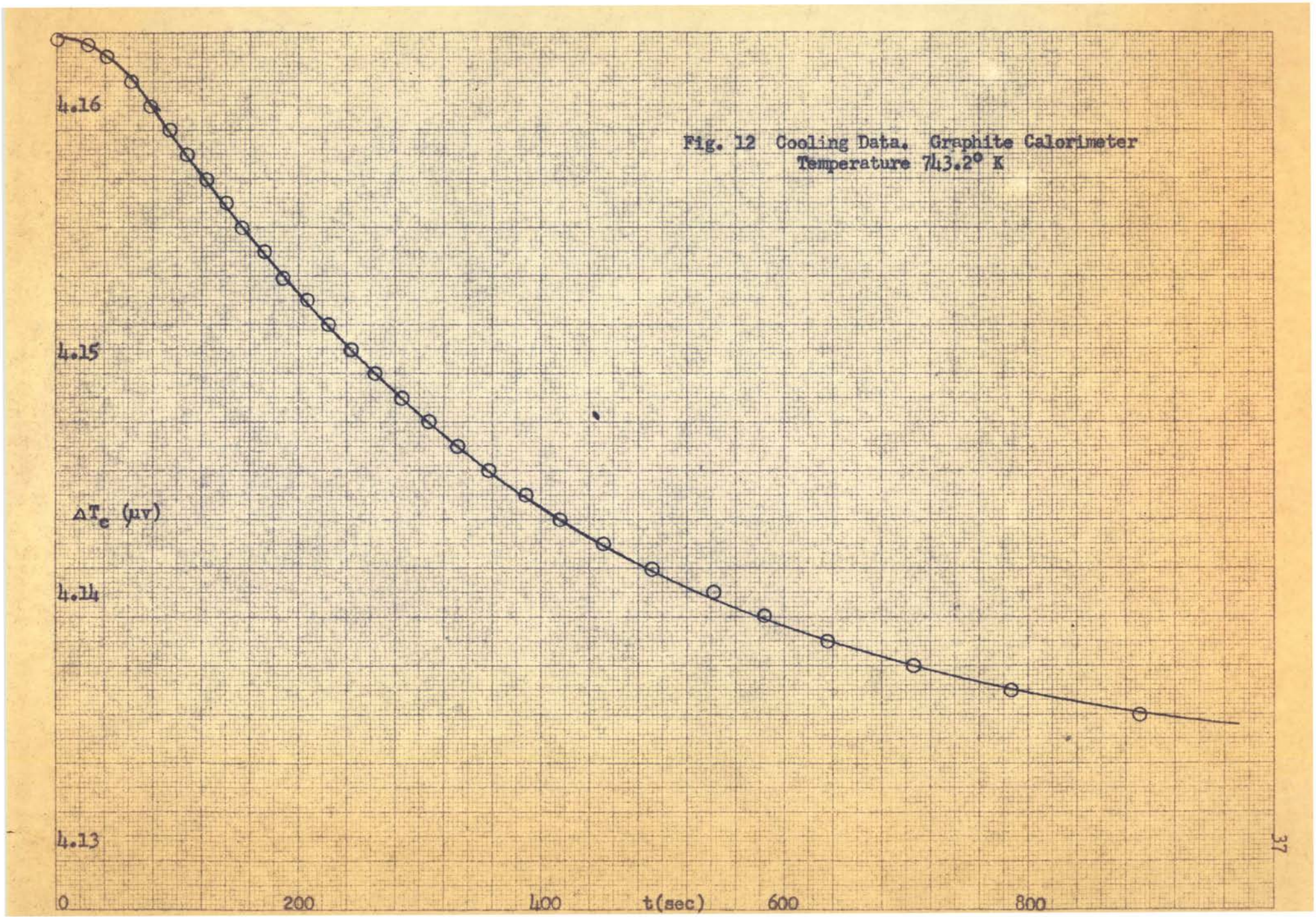
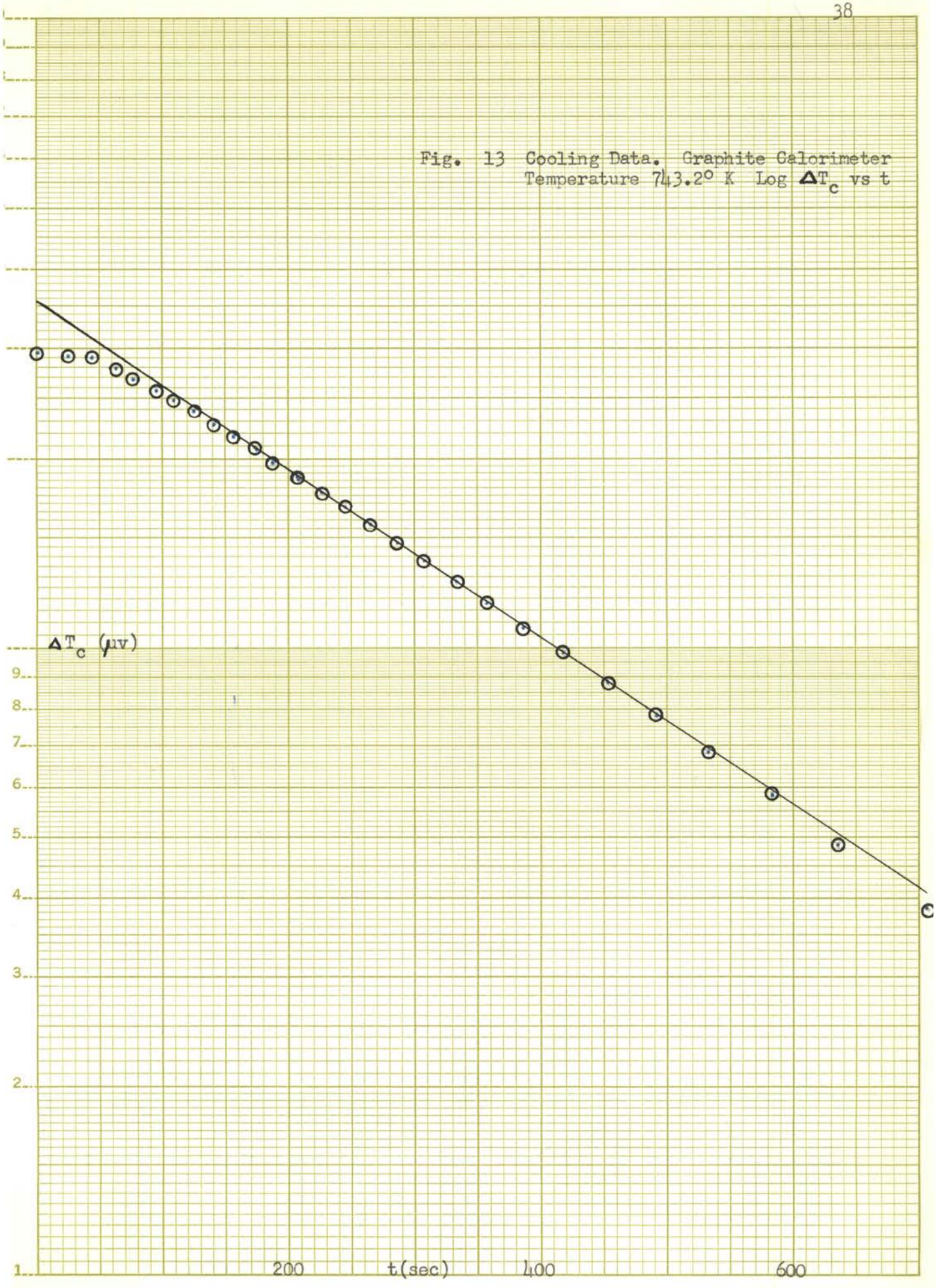


Fig. 12 Cooling Data. Graphite Calorimeter
Temperature 743.2° K

Fig. 13 Cooling Data. Graphite Calorimeter
Temperature 743.2° K Log ΔT_c vs t



V. EXPERIMENTAL

1. Determination of heat capacity.

It is assumed that, when a steady state is reached in the calibration experiments, the conditions will be the same as when the cooling curve reaches the same temperature. This assumption should be valid for materials having high thermal conductance.

From equation (8) it can be seen that the total heat capacity of the calorimeter can be calculated if we know dT_c/dt and q_{cs}. Values of q_{cs} can be readily found at any temperature from the q_{ic} vs ΔT_c graph if the above assumption is correct. The values of dT_c/dt are obtained by taking the slope of the ΔT_c vs t curve at intervals of 100 seconds.

To find the true heat capacity of the calorimeter it is necessary to correct for the heat capacity of the internal heater, electrical leads and pipestem. This corrected heat capacity must then be divided by the number of moles of material in the calorimeter. Therefore the true heat capacity is calculated as follows:

$$\frac{C_p' - \text{heat capacity of internal heater}}{\text{total wt. of calorimeter/mol. wt.}} = C_p \text{ (cal/deg. mole)} \qquad (14)$$

Table 4 shows the computation of the heat capacity of graphite, the data being obtained from the example shown in the theoretical section (Fig. 12 and 13). The heat capacity of the internal heater

was estimated as 0.44 cal./deg. from the weight of the lava (1.580 g.) and the nichrome wire (0.107 g.).

Table 4. Heat capacity of graphite. Temperature 743.2° K. 9.44 moles of graphite.

t(sec)	dT_c/dt(°C/sec)	T_c(μv)	q_{cs}(cal/sec)	C_p(cal/deg mole)
100	6.20×10^{-3}	25.6	0.331	5.60
200	5.07 "	19.2	0.250	5.17
300	4.04 "	14.2	0.185	4.79
400	3.10 "	10.4	0.137	4.63
500	2.26 "	7.6	0.101	4.68
600	1.60 "	5.5	0.074	4.85
700	1.22 "	4.0	0.055	4.72
800	1.03 "	2.8	0.040	4.06
900	0.56 "	1.9	0.028	5.25

K and E mm. paper 50 cm. wide and 45 cm. high was used to plot the cooling curve and calibration data.

It can be seen from the above data that by this method we cannot determine a "single" value of the heat capacity. The reasons, which will be discussed in detail later, are (a) the assumption that $q_{ic}=0$ when $t = 0$ is not valid (b) T_s does not remain constant. Thus the first values are high and the final values are influenced by the drifting shield and may be either high or low.

A method by which a "single" value of the heat capacity can be obtained will be discussed below.

From equation (13) we have seen that a plot of $\ln (T_c-T_c^{\circ})_{t=t}$ vs t should give a straight line whose slope is $\frac{k_{cs}}{C_p}$. By fitting a straight line to a plot of the experimental data (Fig. 13) we are able to obtain the slope. From our calibration data (eq. 9) we can obtain the value of k_{cs}. Knowing the slope of $\ln (T_c-T_c^{\circ})$ vs t and

k_{cs} we can easily find a value for C_p'. Using the calibration data contained in Table 2 and the slope from Fig. 13 one can calculate C_p' to be:

$$\frac{k_{cs}}{\text{slope}} = C_p' = \frac{0.1360}{3.184 \times 10^{-3}} = 42.71$$

and

$$\frac{42.71 - 0.44}{9.44} = 4.49 \text{ cal/deg mole} = C_p$$

2. Heat capacity of graphite.

The heat capacity of a pure sample of graphite has been measured using the method just described. The sample of graphite was National Carbon Company AVC grade having a total ash of 0.02 percent. The impurities were Ca, V, Fe, Ti, Si and S.

Table 5 contains the calibration data obtained.

Table 5. Calibration data. Heat capacity of Graphite

Run no.	T_c	T_s	E_H	E_{std}
1	3.1542	3.1675	0.0000	0.0000
	3.1631	3.1671	1.3576	1.1690
	3.1897	3.1699	2.6134	2.2280
	3.2065	3.1690	3.2454	2.7626
2	3.8655	3.8796	0.0000	0.0000
	3.8741	3.8790	1.5880	1.3507
	3.8842	3.8778	2.3910	2.0333
	3.9021	3.8782	3.2367	2.7490
3	3.2889	3.3001	0.0000	0.0000
	3.3009	3.3006	1.5864	1.3544
	3.3165	3.3004	2.4342	2.0745
	3.3362	3.3008	3.1940	2.7222
4	4.3540	4.3765	0.0000	0.0000
	4.3574	4.3731	1.3894	1.1830
	4.3730	4.3764	2.4870	2.1160
	4.3871	4.3776	3.2054	2.7230

Run No.	T_c	T_s	E_H	E_{std}
5	4.4354	4.4515	0.0000	0.0000
	4.4373	4.4515	1.0922	0.9292
	4.4528	4.4515	2.5389	2.1584
	4.4627	4.4515	3.1150	2.6464
6	5.1166	5.144	0.0000	0.0000
	5.1208	5.144	1.3878	1.1775
	5.1346	5.145	2.7229	2.3076
	5.1372	5.142	3.1384	2.6579
7	5.7888	5.830	0.0000	0.0000
	5.7927	$-\frac{1}{2}$mm*	1.6071	1.3606
	5.7961	5.830	2.3213	1.9637
	5.8060	5.830	3.1960	2.6180
8	5.2700	5.303	0.0000	0.0000
	5.2720	-1mm*	1.2180	1.0348
	5.2797	5.303	2.3104	1.9610
	5.2899	51303	3.1292	2.6534
9	4.1331	4.153	0.0000	0.0000
	4.1485	+1mm*	2.2555	1.9225
	4.1628	-2mm*	3.0654	2.6115
10	3.3526	3.370	0.0000	0.0000
	3.3674	3.370	1.5726	1.3520
	3.3752	3.370	1.9940	1.7090
	3.4014	-1.5mm*	3.2256	2.7536
	3.4012	3.370	3.1859	2.7197
11	2.5291	2.536	0.0000	0.0000
	2.5498	2.538	1.8449	1.6027
	2.5665	-.5mm*	2.4609	2.1282
	2.5809	-.3mm*	2.9036	2.4989

*correction $4\frac{1}{2}$ mm/μv

Table 6 contains the data for the cooling of the calorimeter.

Table 6. Cooling Data. Graphite Calorimeter.

Run No. 1
T_c^o = 3.1542

t(sec)	T_c(mv)	t(sec)	T_c(mv)	t(sec)	T_c(mv)
0	3.2065	123	3.2000	228	20
72	40	188	50	242	10
98	20	202	40	257	3.1900
101	10	215	30	321	60

t(sec)	T_c(mv)
337	50
354	40
371	30
389	20
409	10
428	3.1800
472	80
493	70
516	60
540	50
565	40
615	20
645	10
675	3.1700
742	80
779	70
820	60
862	50
909	40
961	30
1018	20

Run No. 2
T_c^o = 3.8655

0	3.9024
28	20
68	3.9000
82	90
95	80
108	70
120	60
134	50
193	10
208	3.8900
224	90
241	80
257	70
275	60
293	50
355	20
377	10
399	3.8800
423	90
451	80
478	70
538	50
574	40
612	30
657	20

t(sec)	T_c(mv)
706	10
765	3.8700
831	90
916	80
1033	70

Run No. 3
T_c^o = 3.2889

0	3.3362
23	60
45	50
61	40
76	30
89	20
102	10
114	3.3300
139	80
151	70
165	60
178	50
192	40
206	30
220	20
234	10
249	3.3200
297	70
315	60
333	50
351	40
370	30
389	20
410	10
431	3.3100
477	80
501	70
528	60
559	50
621	30
657	20
694	10
633	3.3000
777	90
821	80
872	70
937	60
1002	3.2950

t(sec)	T_c(mv)

Run No. 4
T_c^o = 4.3540

0	4.3869
27	65
39	60
56	50
70	40
84	30
97	20
110	10
124	4.3800
198	50
216	40
231	30
250	20
267	10
289	4.3700
332	80
353	70
375	60
406	50
434	40
465	30
494	20
535	10
576	4.3600
624	90
686	80
739	70
801	60
889	50
1020	4.3540

Run No. 5
T_c^o = 4.4036

0	4.4617
30	15
42	10
60	4.4600
76	90
92	80
107	70
123	60
139	50
154	40
170	30
188	20
204	10

t(sec)	T_c(mv)
224	4.4500
241	90
262	80
285	70
310	60
337	50
365	40
396	30
433	20
470	10
512	4.4400
558	90
607	80
667	70
728	60
820	50
907	4.4340

Run No. 6
T_c^o = 5.1160

0	5.1336
28	35
40	30
59	20
70	10
94	5.1300
111	90
125	80
143	70
151	60
170	50
201	40
222	30
248	20
274	10
304	5.1200
336	90
372	80
415	70
471	60
535	50
616	40
748	30

Run No. 7
T_c^o = 5.7888

0	5.8064
25	60
46	50
65	40
82	30
97	20
115	10
131	5.8000
151	90
173	80
197	70
222	60
249	50
281	40
312	30
354	20
407	10
491	4.7900
610	90

Run No. 8
T_c^o = 5.2700

0	5.2899
32	95
40	90
62	80
79	70
95	60
112	50
128	40
144	30
163	20
182	10
203	5.2800
227	90
251	80
279	70
311	60
350	50
391	40
440	30
505	20
575	10
690	5.2700
884	5.2690

Run No. 9
T_c^o = 4.1331

0	4.1628
26	25
42	20
62	10
77	4.1600
93	90
109	80
123	70
140	60
155	50
172	40
187	30
207	20
225	10
244	4.1400
264	90
286	80
308	70
332	60
358	50
386	40
416	30
451	20
491	10
531	4.1300
583	90
637	80
706	70
785	60
894	50

Run No. 10
T_c^o = 3.3525

0	3.4012
47	3.4000
64	90
78	80
92	70
105	60
119	50
133	40
145	30
158	20
172	10
186	3.3900
201	90
215	80

t(sec)	T_c(mv)	t(sec)	T_c(mv)	t(sec)	T_c(mv)
		Run No. 11		378	2.5600
		T_c^o = 2.5291		400	90
231	70			420	80
247	60			442	70
263	50			463	60
279	40	0	2.5809	487	50
297	30	31	05	511	40
314	20	45	2.5800	539	30
334	10	57	90	565	20
354	3.3800	86	80	596	10
375	90	100	70	622	2.5500
397	80	117	60	652	90
419	70	131	50	685	80
441	60	145	40	721	70
467	50	160	30	751	60
492	40	175	20	790	50
518	30	190	10	827	40
547	20	204	2.5700	868	30
579	10	219	90	910	20
614	3.3700	236	80	957	10
648	90	252	70	1003	2.5400
688	80	268	60		
731	70	286	50		
778	60	304	40		
830	50	322	30		
877	40	339	20		
939	3.3630	360	10		

Table 7 contains a summary of the experimentally determined heat capacity data. Values from K. K. Kelley (1) are listed as a reference. Kelley's values are precise to ± 5%.

Table 7. Heat capacity of graphite.

Run	Temperature °K	C_p	Lit. value	Diff. %
11	587.0	4.26	4.09	+4.2
1	654.0	4.71	4.27	+10.3
3	665.2	4.37	4.30	+1.6
10	668.8	5.12	4.31	+18.8
2	719.7	4.41	4.41	0.0
9	743.2	4.49	4.47	+0.5

Run	Temperature °K	C_p	Lit. value	Diff. %
4	765.4	5.07	4.52	+12.2
5	771.5	4.94	4.53	+9.0
6	833.5	4.60	4.62	-0.4
8	847.3	5.04	4.67	+7.9
7	893.1	5.28	4.75	+11.0

VI. DISCUSSION

1. Internal heater heat transfer.

In the discussion on cooling curves it was noted that a plot of ΔT_c (i.e., $T_c - T_c^{\circ}$) vs. t should give a typical exponential curve. However, the first part of the experimental curve (Fig. 12) does not fall off immediately from the initial point. The curve indicates that the heat flow does not stop abruptly when the internal heater current is switched off. If the heat transfer coefficient between the internal heater and the calorimeter has some finite value, the heater will operate at a higher temperature than the calorimeter. Thus, this effect is caused by the gradual loss of heat from the internal heater after the heater current is switched off.

To analyze this problem, one must consider a more general equation of the apparatus than that given in (1). The equation is:

$$qi - C_i \frac{dT_i}{dt} - C_p' \frac{dT_c}{dt} - q_{is} - q_{cs} = 0 \qquad (15)$$

where q_i = heat being generated in the internal heater winding by electric current

C_i = effective heat capacity of the internal heater

T_i = temperature of the internal heater

T_c = temperature of calorimeter

C_p' = heat capacity of calorimeter

q_{is} = heat loss from internal heater to shield via heater lead wires

q_{cs} = heat loss from calorimeter to shield

Under steady state conditions the derivatives in equation (15) will be zero and the equation will reduce to $q_i - q_{is} - q_{cs} = 0$ during calibration. The lead wires to the heater are small and it seems a reasonable assumption that q_{is} will be a small fraction of q_{cs} and thus $q_i = q_{cs}$. These were the conditions that were originally postulated as being necessary for correct correlation between the calibration and cooling curve data.

Under cooling conditions where $q_i = 0$, if we assume $q_{is} = 0$ the basic equation becomes:

$$-C_i \frac{dT_i}{dt} - C_p' \frac{dT_c}{dt} = q_{cs} \tag{16}$$

T_i will be higher than T_c. If we set $T_i - T_c = h$ we can write equation (16) as:

$$-C_i \frac{dh}{dt} - (C_i + C_p') \frac{dT_c}{dt} = q_{cs} \tag{17}$$

or

$$C_i + C_p' = -\frac{q_{cs}}{dT_c/dt} - C_i \frac{dh/dt}{dT_c/dt} \tag{18}$$

If the apparent heat capacity C" is taken equal to $-\frac{q_{cs}}{dT_c/dt}$, then

$$C'' = C_i + C_p' - C_i \frac{dh/dt}{dT_c/dt} \tag{19}$$

As the cooling progresses h (i.e., $T_i - T_c$) will rapidly approach zero and thus cause the third term on the right hand side of equation (19) to become insignificant. Therefore, the apparent heat capacity will soon approach the value of the heat capacity of the calorimeter plus that of the internal heater.

There are two ways in which the internal heater effect can be minimized: (1) by reducing the effective heat capacity of the

internal heater and (2) by reducing the difference in temperature $(T_i - T_c)$.

The effective heat capacity of the internal heater was reduced by making the lava heater form small and with very thin walls. The nichrome heater wire size was also reduced.

To reduce the temperature difference $(T_i - T_c)$ it was necessary to make good thermal contact between the internal heater and calorimeter. The plug fitted inside the internal heater that made contact with the calorimeter at both ends facilitated the heat transfer. The space between the wire winding and the calorimeter (graphite) was packed with powdered Magnorite (trade name for synthetic periclase). This increased the rate of heat transfer at low temperature differences but at higher temperatures, where apparently radiation is more important, it hindered heat transfer. Thus, overall, the Magnorite interfered with the heat transfer and added to the effective heat capacity of the internal heater.

It might be possible to construct an internal heater that would be only a wire heating element wound on a cross of thin mica sheets for support. The effective heat capacity of a heating element of this type would be very small and at temperatures high enough for radiation heat transfer, the transfer coefficient would be large.

2. Internal heater heat loss to shield.

In section (1) above the assumption was made that the wire heater leads were small and that the heat leak (q_{is}) along them to the shield was negligible compared to the heat transfer between the calorimeter and the shield (q_{cs}). If this assumption is not correct

then at steady conditions:

$$q_i = q_{is} + q_{cs} \tag{20}$$

and our calibration conditions will not be the same as the cooling curve conditions at the same temperature. Thus $q_i > q_{cs}$ and the value C_p' obtained in the calculation, on the assumption that $q_i = q_{cs}$ will be too large. An evaluation of this effect has not been satisfactorily made at this time.

3. Calibration data.

We have previously set $k_{cs} = 4\sigma A g T_a^3 + K_N$ and thus a plot of k_{cs} vs T_a^3 should give a straight line with a slope equal to $4\sigma Ag$, if the assumption that g, A and K_N were constant is correct.

Figure 14 shows a plot of k_{cs} vs T_a^3. From the data it appears that it would be better to draw two straight lines through the experimental data. Using the slopes of the straight lines through the data and an approximate estimation of $4\sigma A \simeq 4.41 \times 10^{-10}$ we calculate g to be:

$$\text{line 1.} \qquad g = \frac{3.50 \times 10^{-10}}{4.41 \times 10^{-10}} = 0.794$$

$$\text{line 2.} \qquad g = \frac{3.78 \times 10^{-10}}{4.41 \times 10^{-10}} = 0.857$$

These values are of the correct order of magnitude and indicate that the assumption $4\sigma Ag$ is a constant was correct. However, the intercept of the two lines indicate that the value of K_N increases abruptly between 771 and 833°K.

It has been observed that, at high temperatures (about 700° K) considerable graphite sublimed and collected on various parts of the

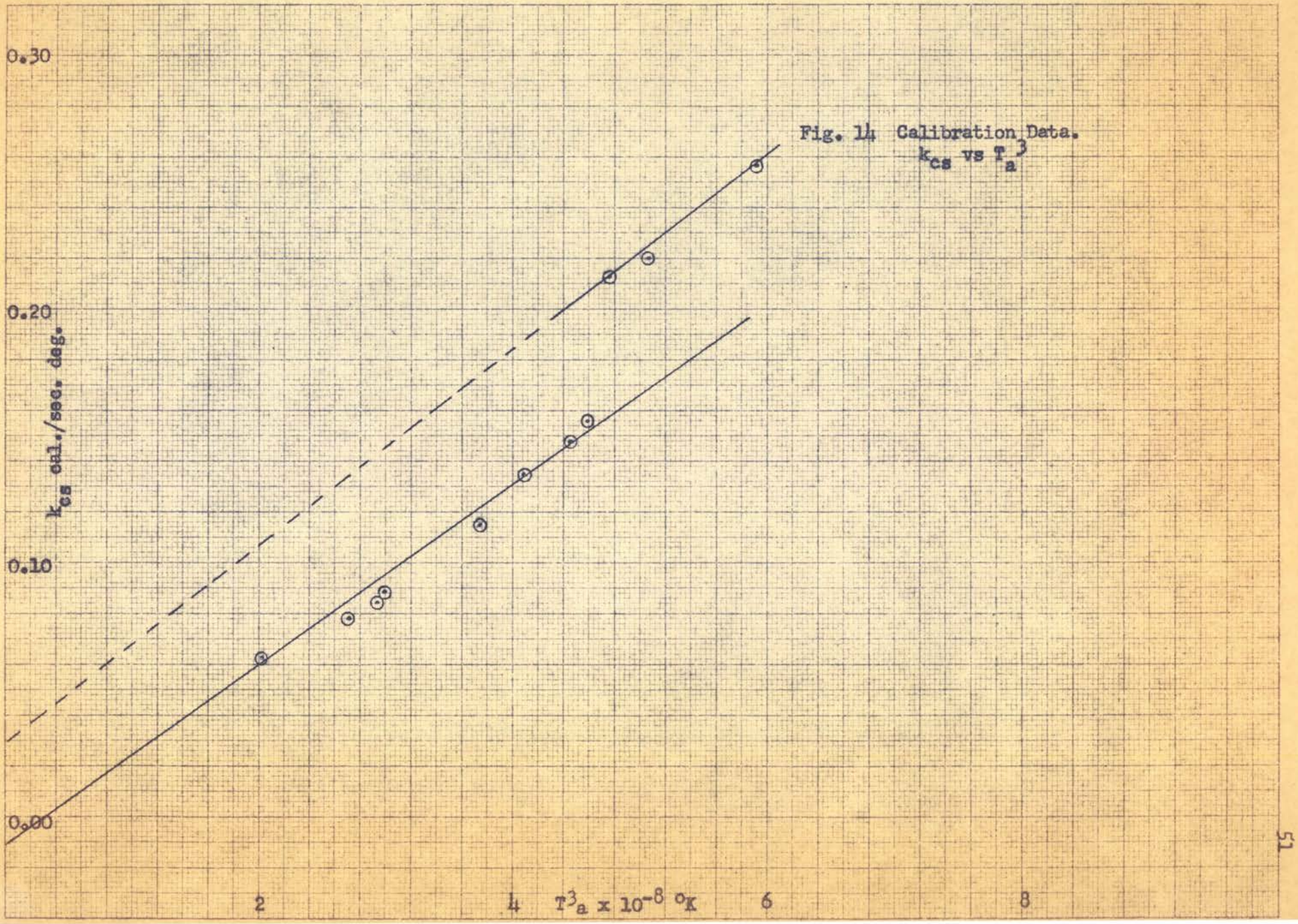


Fig. 14 Calibration Data.
k_{cs} vs T_a^3

apparatus. If sufficient graphite was sublimed, to reduce the pressure inside of the shield furnace, there would be an additional loss by convection.

Another possibility would be an increase in thermal conductivity of the lava supports and ceramic insulators at higher temperatures. However, we would not expect this change to be quite so abrupt.

4. Shield furnace.

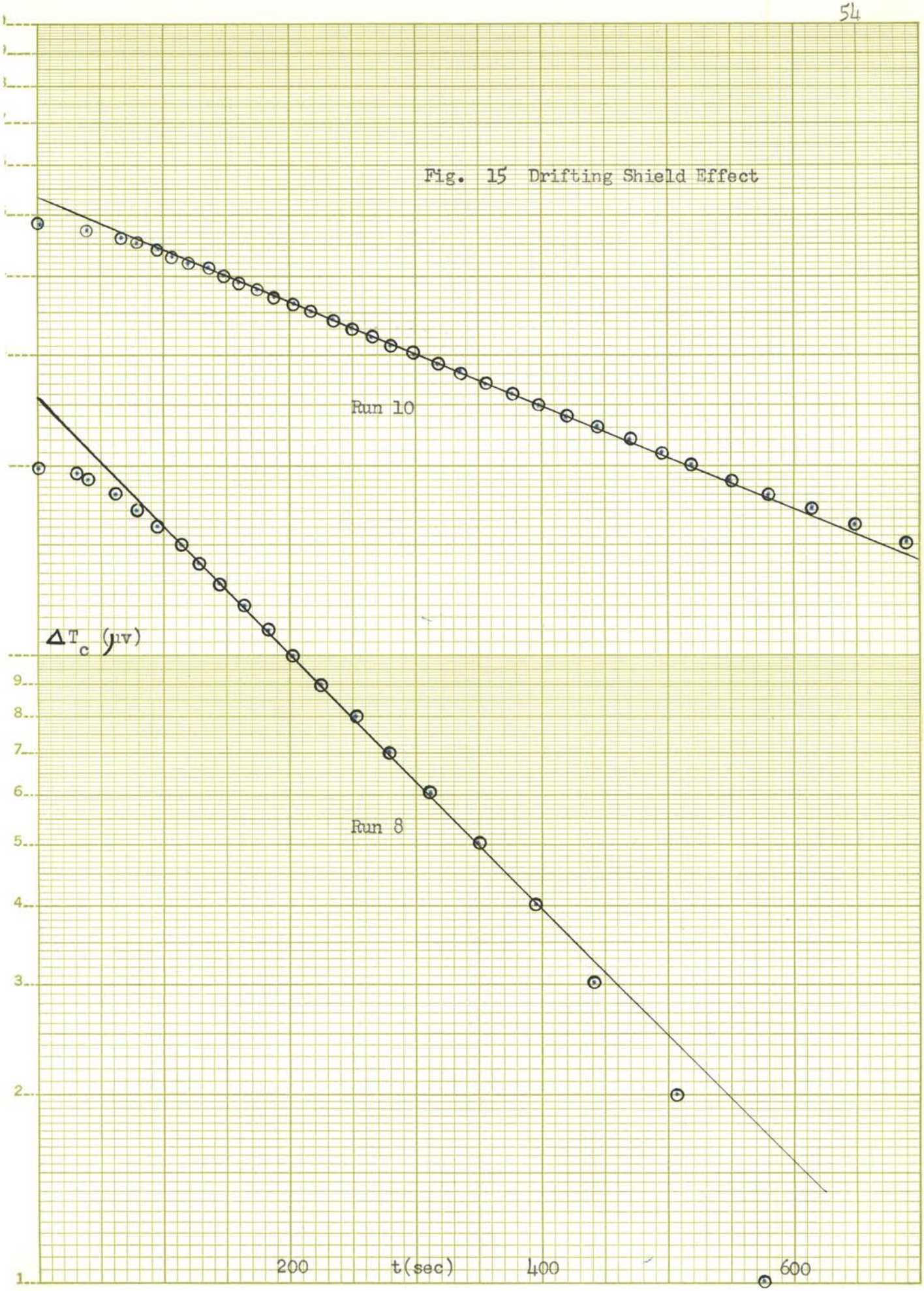
During these experiments various attempts have been made to maintain the shield furnace at a constant temperature. However, because of the furnace lag, it has not been possible to achieve perfect temperature control. Thus we have been plagued by internal heater trouble at the beginning of the cooling curve and drifting shield at the end of the cooling curve. Because of the temperature gradient across the furnace it appears that one means of controlling the shield furnace temperature would be to use a heater element that could also be used as a resistance thermometer. By means of a signal directly from the heater itself it might then be possible to automatically control the shield furnace at a constant temperature.

5. Precision of the heat capacity data of graphite.

The heat capacity of graphite determined by the method outlined in the experimental part of this thesis has not been precise because the desired temperature control was not realized. During most of the calibrations the shield continually oscillated about the desired temperature because the electromagnetic voltage stabilizer did not completely smooth out the fluctuations in line voltage. Therefore the ideal steady state conditions were not obtained during the calibration.

Furnace shield temperature was not kept constant during the entire cooling run and the cooling temperature of the calorimeter was influenced by the drifting shield during the later part of the run. This is shown in Figure 15 Run 10 the temperature of the shield increased + 3 μv and in run 8 the temperature decreased - 4 μv.

Fig. 15 Drifting Shield Effect



VII. SUMMARY

Improvements in the construction and operation of a radiation calorimeter have been made.

To assure a more constant voltage source to the internal heater, three automobile storage batteries connected in parallel were utilized in place of the one previously used.

Installation of a safety device in the diffusion pump circuit (which turned the diffusion pump off when the water pressure dropped to a set level) made it possible to operate the vacuum system continuously. Convection effects were thereby minimized.

A more sensitive galvanometer was used in measuring the temperature of the calorimeter. This gave greater precision in the measurement of the temperature of the calorimeter during a cooling curve run.

The shield furnace was improved by (a) construction of a spherically symmetrical graphite liner with a surface of uniform emissivity (b) the shield heater wire in an alundum shell that made good thermal contact with the graphite liner and thus assuring uniform temperature at the inner surface of the shield furnace.

A thyratron control circuit was constructed to keep the shield temperature at a constant value. Fruitless attempts were made to construct a device which would control the temperature automatically within the desired limits. However, by manual control, the variation in temperature of the shield during calibration was kept to $\pm 0.001^{\circ}$

at 673° C. Control of the shield during cooling of the calorimeter was more difficult, however, and the shield temperature was controlled only to ±0.15° toward the end of the cooling curve.

Numerous measurements of the heat capacity of graphite have been made during the period of this study. The values obtained for the heat capacity indicate that additional refinements are needed to increase the precision of the calorimeter.

The experimental evidence obtained justifies the theoretical calculations governing the operation of the calorimeter. Better control of the shield furnace, to obtain greater precision in the cooling curve data, and an accurate determination of the heat loss from the heater to the shield, to correct the calibration data, will make the radiation calorimeter described herein a valuable tool in the study of metals and alloy systems.

With additional sutdies it should be possible to develop a hollow calorimeter, to contain liquid materials for which heats of reaction, heats of solution (e.g., molten metals) and heats of transition at high temperatures could be determined.

BIBLIOGRAPHY

1. Kelley, K. K., Contributions to Data on Theoretical Metallurgy. X. Bureau of Mines Bulletin 476, U. S. Govt. Printing Office, Washington D. C., 1949. pp. 2 and 45.

2. White, W. P., Jour. Phys. Chem., 34, 1121 (1930).

3. Willis, W. R., A Radiation Calorimeter: The Heat Capacity of Graphite, Unpublished Ph. D. Thesis, Oklahoma A. and M. College, 1953.

4. Jaeger and Diesselhorst, Wiss. Abhandl. physik. tech. Reichsanstalt, 3 (1900).

5. Lecher, Verhandl. deut. physik. Ges., 9, 647 (1907).

6. Corbino, O. M., Physik. Z., 13, 375 (1912).

7. Pirani, M. R., Verhandl. deut. physik. Ges. 14, 1037 (1912).

8. Worthing, A. G., Phys. Rev., 12, 199 (1918).

9. Behrens, W. U. and C. Drucker, Z. physik. Chem., 113, 79 (1924).

10. Gaede, W., Physik. Z., 4, 105 (1902).

11. Sucksmith and Potter, Proc. Roy. Soc. (London), 112, 157 (1926).

12. Klinkhardt, Z. Elektrochem., 32, 534 (1926).

13. Grosse, W. and W. Dinkler, Stahl u. Eisen, 47, 448 (1927).

14. Carpenter, L. C., Proc. Phys. Soc. (London), 44, 383 (1932).

15. Newton, R. F., B. D. Kaura and T. DeVries, Ind. Eng. Chem., 23, 35 (1931).

16. Kubaschewski, O. and coworkers, Z. Elektrochem., 45, 630 (1939).

17. Wittig, F. E., Z. Elektrochem., 54, 288 (1952).

18. Knappworst, A., Z. Elektrochem., 49, 1 (1943).

19. Williams, J. W. and F. Daniels, J. Am. Chem. Soc., 46, 903 (1924).

20. Richards, J. W., Proc. Am. Acad. Arts and Sci., 41, 2 (1905).

21. Kangro, W., Z. Elektrochem., 34, 235 (1928).

22. Sykes, C., Proc. Roy. Soc. (London), 148, 422 (1935).

23. Sykes, C. and H. Evans, J. Inst. Metals, 58, 255 (1936).

24. Sykes, C. and F. W. Jones, J. Inst. Metals, 59, 257 (1936).

25. Sykes, C. and H. Wilkinson, J. Inst. Metals, 61, 223 (1937).

26. Sykes, C. and H. Evans, J. Iron Steel Inst. (London), 138, part II, 125 (1938).

27. Swindells, N. and C. Sykes, Proc. Roy. Soc. (London), 168, A, 237 (1938).

28. Moser, H., Physik. Z., 37, 737 (1936).

29. Quinney, H. and G. I. Taylor, Proc. Roy. Soc. (London), 163, A, 157 (1937).

30. Winkler, J. R., J. Am. Ceram. Soc., 26, 339 (1943).

31. Stow, F. S. and J. H. Elliot, Anal. Chem., 20, 250 (1948).

32. Armstrong, L. D., Can. J. Research, 28, A, 44 (1950).

33. McKisson, R. L. and L. A. Bromley, A New High-Temperature Calorimeter, United States Atomic Energy Commission, Technical Information Division, ORE, Oak Ridge, Tenn., May 1, 1950.

34. Malcolm, D. and coworkers, Rev. Sci. Inst., 22, 812 (1951).

35. Rolser, W. M. and H. T. Wensel, J. Research Nat. Bur. Standards, 14, 247 (1935).

36. Goodsave, G. A. E., A Note on Radiation Heat Transfer. Memo 111, National Gas Turbine Establishment (March 1951).

37. McAdams, W. H., Heat Transmission, McGraw-Hill Book Co., New York, 1942.

VITA

Wynn B. Fife
candidate for the degree of
Doctor of Philosophy

Thesis: A STUDY OF FACTORS AFFECTING OPERATION OF A RADIATION CALORIMETER

Major: Chemistry

Biographical and Other Items:

Born: The writer was born in Brigham City, Utah, June 24, 1919, the son of Basil C. and Winifred B. Fife.

Undergraduate Study: He attended Utah State Agricultural College and obtained a Bachelor of Science degree in Chemistry in 1948.

Graduate Study: A Master of Science degree in Chemistry was obtained at Utah State Agricultural College in 1951. In September of 1950 he entered the Graduate School of Oklahoma A. & M. College. Requirements for the Doctor of Philosophy degree in Chemistry were completed in August, 1953.

Experiences: The writer volunteered for duty in the United States Air Force July, 1942. He was given an honorable discharge in September of 1946. Since this time he has been attending college.

Member of Phi Lambda Upsilon and the American Chemical Society.

Date of Final Examination: August, 1953.

THESIS TITLE: A Study of Factors Affecting Operation of A Radiation Calorimeter

AUTHOR: Wynn B. Fife

THESIS ADVISER: Dr. Irving Johnson

The content and form have been checked and approved by the author and thesis adviser. The Graduate School Office assumes no responsibility for errors either in form or content. The copies are sent to the bindery just as they are approved by the author and faculty adviser.

TYPIST: Mrs. J. O. Richardson